Navy Small Business Innovative Research Program

Oxygen Source for Underwater Vehicle Fuel Cells
(Final Report)

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14. Abstract

Report developed under STTR contract for topic N01-T005. Four successful tests were conducted to demonstrate the usefulness of lithium oxide as a catalyst and manganese as a fuel for the release of oxygen by the decomposition of lithium perchlorate at low temperature. The test apparatus included two stainless vessels, one to hold molten lithium perchlorate and the other the reaction vessel. The molten perchlorate was fed to the reaction vessel using dry nitrogen gas as a driver. Two tests were conducted using lithium oxide as a catalyst with the reaction chamber at 1,000°F. Both tests produced oxygen immediately upon introduction of 600°F lithium perchlorate. These tests lasted for eight and thirteen minutes. Two additional tests were conducted using a mixture of manganese and lithium oxide in the reaction vessel at 600°F. In both cases there was an immediate, significant temperature increase indicating oxidation of the manganese. The feed nozzle plugged during both manganese tests, most likely due to lithium perchlorate decomposition in the nozzle due to high temperature. The report includes a go forward plan for additional quantifying tests.

1. SUMMARY

Barber-Nichols Inc, with support from ARL/Penn State, conducted tests to demonstrate the benefit of the use of lithium oxide as a catalyst and manganese as a fuel in triggering the decomposition of lithium perchlorate at reduced temperatures. Oxygen gas (for use in underwater vehicle fuel cells) is the desired product produced during lithium perchlorate decomposition. Successful tests were conducted at 1000°F with the catalyst and at 600°F with the fuel and catalyst. Without the use of these additives, sustained perchlorate decomposition requires initial temperatures near 1200°F. These tests were conducted for ONR STTR topic N01-T005, contract N0001-01-M-0210.

2. BACKGROUND

Oxygen is the most abundant element on Earth, making up approximately 50% of the planet's mass (Ardon, 1965). Oxygen plays a proportionally large role in many biological and chemical processes; for example, normal human respiration requires several pounds of O_2 daily (Benton, 1970). Commercial and medical uses of oxygen are widespread, requiring approximately 20 million tons of O_2 annually (Lide, 1993).

One of the most important applications for O_2 is its use as an oxidizer to convert the chemical potential energy of fuels to thermal, mechanical, and/or electrical energy. In addition to its use as an oxidant in combustion applications, oxygen can be combined with hydrogen or hydrocarbon fuels in a fuel cell, which produces electricity directly from an electrochemical reaction without combustion. In most terrestrial fuel cell processes, the source of oxygen is the atmosphere, which contains approximately 21% O_2 on a molar basis. In undersea applications (as well as some aerospace and medical processes) an alternate source of oxygen is required.

Pure oxygen is produced primarily through air separation and is stored and shipped as a liquid or compressed gas. Liquid oxygen (LOX) has a critical point temperature of 154.58 K (-181 °F). Thus, cryogenic O_2 storage entails bulky insulated tanks and necessitates continuous venting of gas to the atmosphere. Pressurized oxygen gas requires massive cylinders, and since high-pressure oxygen can react violently with organic materials, specially cleaned fittings are required (CGA, 1987). Under the proper conditions, most materials (including metals) will burn in oxygen. Sources of ignition associated with LOX and/or high-pressure oxygen gas include adiabatic compression heating, frictional heating, mechanical impact of particles carried by high velocity gas flows, and static discharge (Dees et. al.).

Hydrogen peroxide (H_2O_2) has been used as an oxygen source in a number of terrestrial and underwater applications. Because hydrogen peroxide decomposes spontaneously, it is necessary to continuously vent oxygen to avoid overpressurization of peroxide storage tanks. Although recent advances in passivation techniques have improved the stability of concentrated peroxide and addressed some of the safety hazards that have historically been associated with this material, its sensitivity to temperature and contamination

remains a concern (Clark, 1972). There is evidence that the August, 2000 sinking of the Russian submarine Kursk was caused by an explosion in a torpedo H_2O_2 oxidizer tank (Isachenkov, 2002).

Oxygen candles are frequently used as an emergency source of O_2. In these devices, an oxygen-containing chemical (typically sodium chlorate, $NaClO_3$) is pressed into a solid grain with a sub-stoichiometric quantity of a metallic fuel, such as iron. When initiated, a portion of the chlorate reacts with the fuel to produce heat, which causes the remainder of the $NaClO_3$ to decompose, releasing oxygen through the chemical reaction;

$$NaClO_3 \text{ -----> } NaCl + 1.5\ O_2 \qquad [1]$$

In life support applications, a filter and scrubber are necessary to remove NaCl particles and traces of chlorine gas. Candles are used as a reliable source of oxygen in a number of military and civilian aerospace applications. Unfortunately, as with other systems that incorporate pyrotechnic grains (solid rocket motors, for example), there is no convenient way to modify the burn rate or stop the reaction once initiated. In addition, the grain is a pyrotechnic, requiring careful handling and installation to avoid unintentional ignition. The recent crash of a commercial passenger jet in the Florida Everglades has been tentatively attributed to the unintentional ignition of oxygen generator cartridges being transported in the cargo hold. (NTSB, 1997).

Each of the oxygen storage options described above has inherent limitations. There is a need for a dense controllable oxygen source that can be used in applications where cryogenic or high-pressure storage options are impractical.

2.1 Chemical Oxygen Sources: $LiClO_4$

As discussed above, oxygen can be stored and transported as a pure liquid or a high-pressure gas. An alternative "storage" mechanism is to use a chemical reaction to generate O_2. Figure 1 shows the amount of oxygen that can be produced for a given volume of a number of oxygen rich chemicals. Most of these materials produce oxygen through decomposition reactions similar to the oxygen candle process (see equation [1]). An exception is sodium peroxide, which yields O_2 when it reacts with water, i.e.;

$$Na_2O_2 + H_2O \text{ ----> } 2NaOH + 1/2O_2 \qquad [2]$$

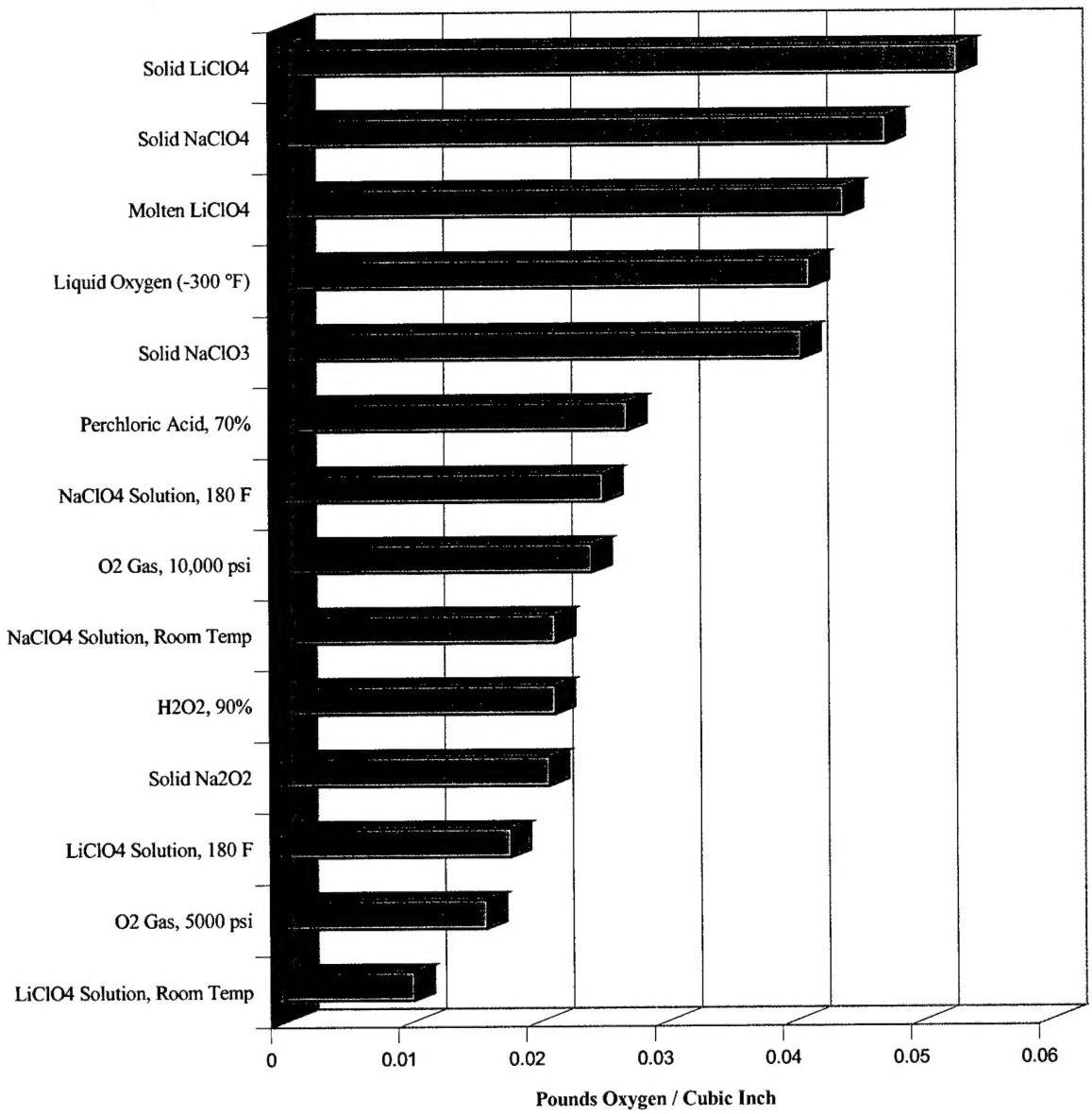
The most oxygen dense species shown in Figure 1 is lithium perchlorate, or $LiClO_4$. In its solid form, this substance contains 28% more oxygen than an equivalent volume of liquid oxygen (measured at the LOX boiling point temperature; -300 °F). The extreme oxygen density of lithium perchlorate has long focused attention on this material as an oxygen source. For example, a candle formulation containing $LiClO_4$ and manganese fuel was developed in the mid 1960's (Markowitz and Dezmelyk, 1964: Markowitz, et. al., 1964).

Lithium perchlorate produces oxygen through the decomposition reaction;

$$LiClO_4 \text{ ----> } LiCl + 2O_2 \qquad [3]$$

The rate of this reaction is highly temperature dependent. One source (LCA, 1958) characterizes the rate of decomposition as "Slight" at temperatures below 600 °F, "Rapid" at 774 °F, and "Violent" at 945 °F. In reality, the decomposition kinetics are more difficult to characterize than this simple model would suggest. Reaction [3] is catalyzed by the presence of the lithium chloride product (Solymosi and Braun, 1967: Cordes and Smith, 1974). The process therefore accelerates as it goes to completion. This autocatalytic phenomenon is exacerbated by the fact that the decomposition reaction is slightly exothermic (ΔH_{RXN} = -244 BTU/lb at the melting point of $LiClO_4$; 457 °F).

Figure 1. Oxygen Storage Alternatives



Lithium perchlorate appears to be the only alkali metal perchlorate with a liquid phase that is stable at temperatures significantly above its melting point. Although there is some discrepancy in the literature regarding the decomposition behavior of sodium perchlorate (Markowitz et. al, 1961), more recent data indicates that $NaClO_4$, like the potassium, rubidium and cesium salts, decomposes at temperatures below (or congruent with) its melting point (Solymosi and Braun, 1967: Lide et. al., 1993).

2.2 ARL Molten Perchlorate Oxygen Generators

ARL has developed a "Steady Flow Oxygen Generator," shown schematically in Figure 2. In this device, a bath of liquid lithium perchlorate is held in a "storage vessel" at a relatively low (i.e.550 – 600 °F) temperature. Under these conditions, the rate of decomposition is minimal. The liquid perchlorate is pumped into a separate chamber (the "reaction vessel") and sprayed against a heated surface, which causes it to decompose instantaneously. The rate of oxygen production is varied simply by controlling the rate at which perchlorate is transferred into the reactor section. By using two chambers with different operating temperatures, the ARL liquid perchlorate based oxygen generator capitalizes on the rapid decomposition kinetics and autocatalytic nature of the decomposition process, while still maintaining the bulk of the molten material in a relatively stable form.

The transfer of perchlorate from the storage chamber into the reaction chamber can be accomplished through mechanical pumping or by increasing the storage vessel pressure to apply a hydrostatic head. The appropriate pumping mechanism for a particular application depends on the scale of the system, its operating pressure, and the rate of oxygen flow required. Both hydrostatic and mechanical (piston and gear pumps) have been demonstrated.

Figure 3 shows a large-scale oxygen generator developed at ARL. Using this and similar devices, ARL has investigated the use of perchlorate based oxygen generators for use in high-speed underwater vehicles powered by combustion reactions. Over 60 experiments have been performed at a wide range of oxygen flowrates and delivery pressures. The largest systems evaluated to date produced approximately 30 kg (66 lb) of oxygen at flowrates as high as 114 kg/hr (0.07 lb/sec).

As discussed above, the rate of oxygen production can be controlled by varying the rate at which perchlorate is transferred from the cool storage vessel to the reaction chamber. Figure 4 shows data taken during an experiment. Note that excellent control was realized over a wide range of flowrates.

A patent (Peters et. al., 1994) has been obtained for the basic two-chamber steady flow oxygen generator apparatus. This patent has been allowed to lapse and is now in the public domain.

Figure 2: ARL Molten Perchlorate Oxygen Generator

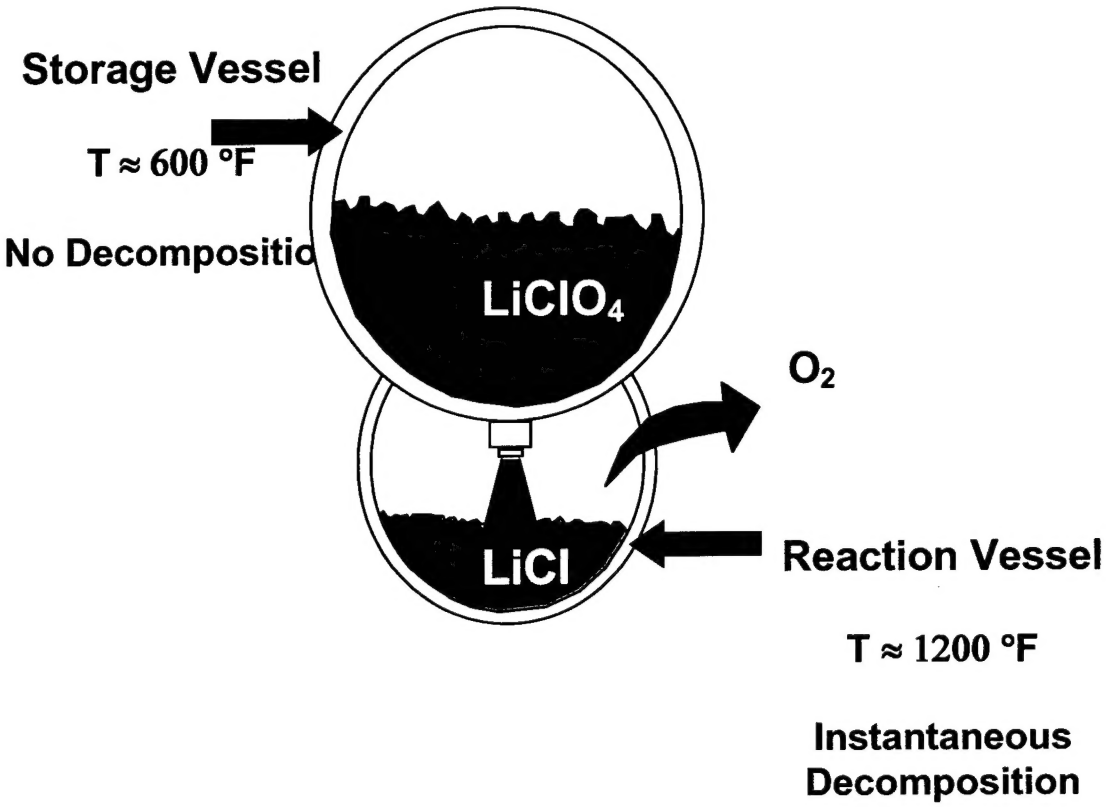
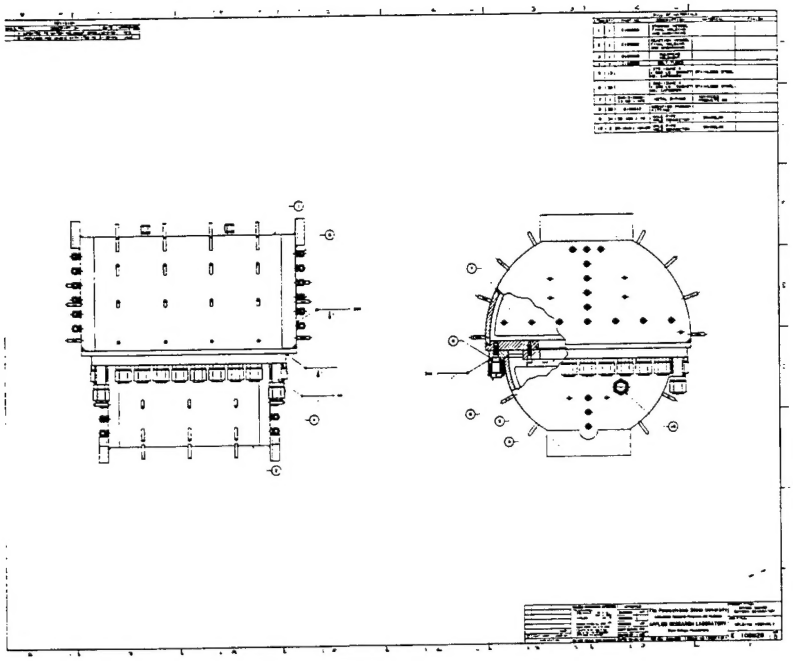


Figure 3: ARL Large Scale Oxygen Generator; Delivers 66 Pounds Oxygen Gas



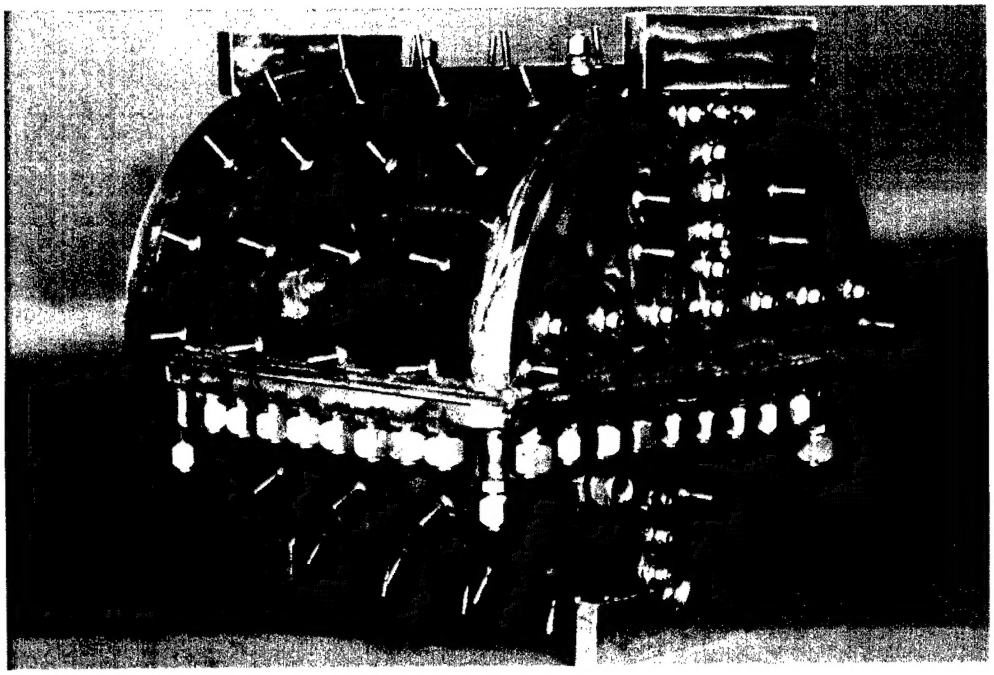
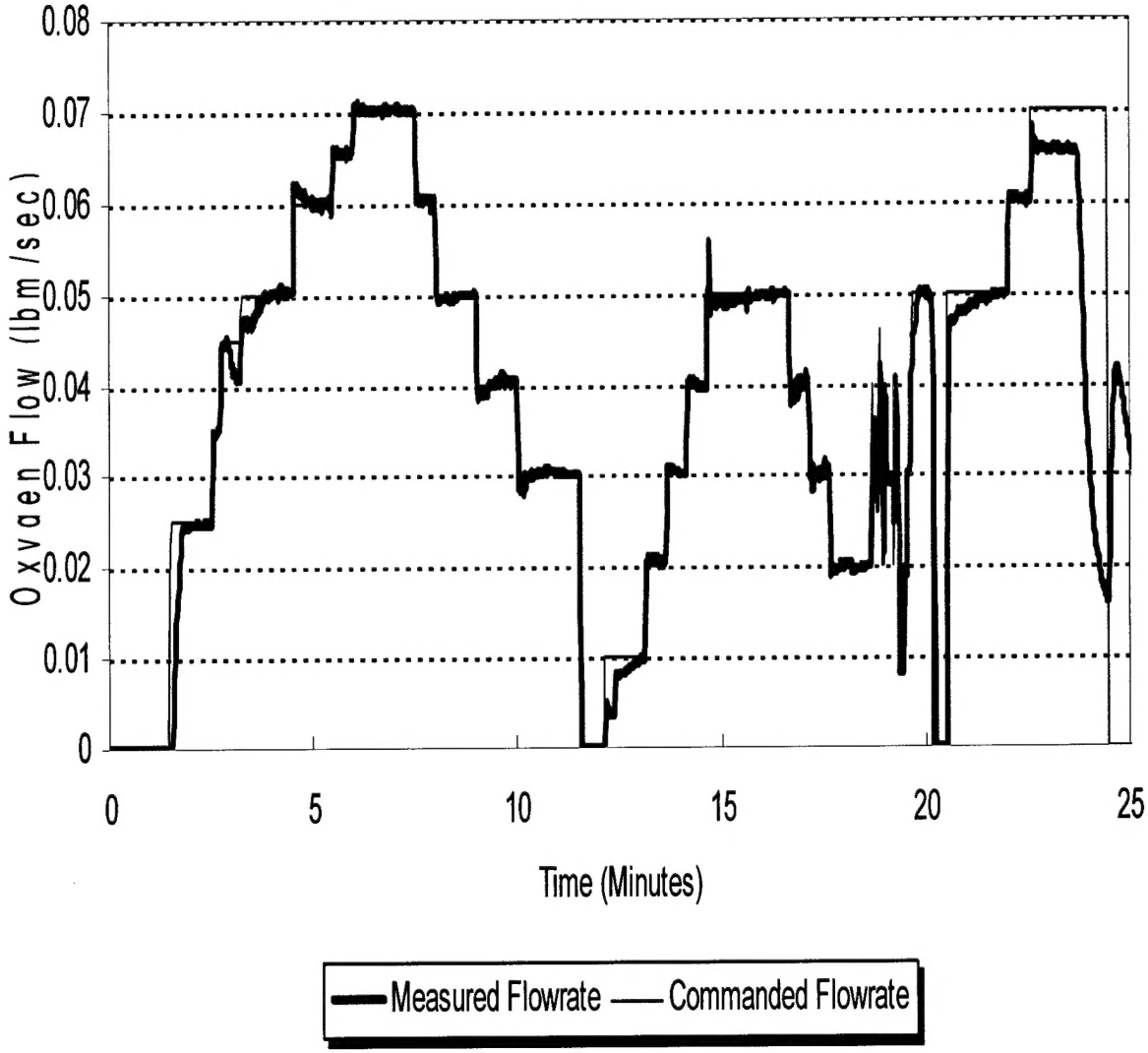


Figure 4: Measured vs. Commanded Flowrate for ARL Oxygen Generator Experiment #53



3. DESCRIPTION OF PROGRAM

As discussed above, efforts to develop a perchlorate based oxygen generator have thus far focused on high-speed underwater propulsion applications. The present proposal is addressed at a relatively low rate (e.g. 100 grams/minute oxygen flow) long duration (e.g. 40 – 60 hour) UUV application.

3.1 Technical Issues

The low speed long duration nature of the UUV application imposes several technical challenges, summarized below;

1. In existing oxygen generators sized for high-speed applications, the lithium chloride product is contained in the reaction vessel. This requires a sizeable reaction vessel volume. In optimal low-rate designs, it will be necessary to minimize the reaction vessel volume by removing the chloride product from the reaction vessel as it is formed.

   This process is complicated by the fact that the LiCl is in a molten state at normal reaction vessel operating temperatures, leading to plugging downstream of the reaction vessel as the liquid chloride freezes in the exhaust line.

2. The chloride product must be converted into a form that can be discharged overboard in a manner that reduces or eliminates parasitic energy losses and the formation of detectable gaseous or chemical wakes.

3. The long duration nature of the application makes it necessary to reduce the amount of energy needed for startup and heat lost during operation to as large an extent as possible.

3.2 Technical Approach

The experimental program described in this report focused on the use of a catalytic material, lithium oxide (Li_2O), and the metallic fuel manganese (Mn) to address the technical issues outlined above. In the experiments outlined in the following section, the decomposition chamber initially contained lithium oxide or a mixture of Li_2O and Mn.

As has been demonstrated with $LiClO_4$-based oxygen candles, manganese is an effective fuel for oxidation with molten perchlorate. (Markowitz and Dezmelyk, 1964; Markowitz, Boryta and Stewart, 1964). Thus, the initial spray of molten $LiClO_4$ reacts with Mn, serving as a "quick-start" heating process to raise the operating temperature of the chamber to approximately 1000 °F. Only enough manganese will be added to sufficiently heat the chamber; once that is accomplished, the normal decomposition reaction will proceed. Note that once the manganese is spent, the remaining MnO_2

product acts as a catalyst for perchlorate decomposition, enabling faster kinetics and operation at a lower (1000 °F) temperature (Markowitz and Boryta, 1965).

Lithium oxide not only is an effective catalyst for the decomposition reaction (Nikitina and Rosolovskii, 1997) but also retards the formation of Cl_2, especially in the presence of MnO_2 (Markowitz, Boryta and Stewart, 1964).

Although existing reaction vessel designs rely on the presence of the liquid LiCl bath to catalyze the decomposition reactions, it appears from the studies cited above that Li_2O has the potential to be a more effective catalyst. The presence of the Li_2O and MnO_2 catalysts therefore allows operation at temperatures below the melting point of LiCl. Lower reaction vessel temperature would address the technical issues outlined above as follows.

1. Operation at temperatures below the melting point of the lithium chloride product (1130 °F), should reduce exhaust line plugging, as solid chloride particles should have a lower tendency to stick to the colder downstream components (i.e. exhaust tube, venturi separator walls, control valve) than molten LiCl droplets.

2. The lithium chloride is ultimately discharged from the system. For this reason, the thermal energy associated with cooling this product to ambient conditions represents a net loss to the system. Colder solid products therefore result in a lower heat transfer to the environment.

3. Colder reaction vessel and exhaust components will lose less heat through conduction to the environment.

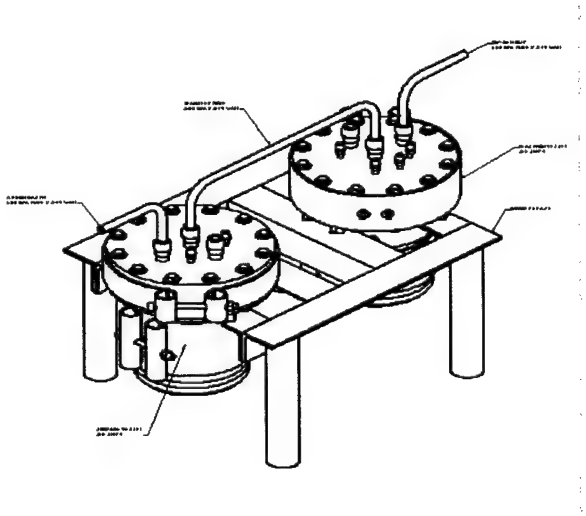
4. The use of Mn fuel should allow the reaction vessel to start at the same initial temperature as the storage vessel, simplifying the pre-heat process.

4. TEST PROGRAM

The goal of the test program was to demonstrate the effectiveness of lithium oxide as a catalyst and manganese powder as a chemical heat source for generating oxygen from lithium perchlorate. The test results were to be more qualitative than quantitative in nature. Further testing will be necessary to fully define and map the performance potential of lithium perchlorate based oxygen generators.

4.1 Apparatus

The test apparatus used was modeled closely to apparatus previously tested at the Applied Research Laboratory (ARL, Penn. State Univ.). The test apparatus (oxygen generator) consisted principally of two vessels of similar construction. The "storage" vessel initially holds the lithium perchlorate that is later transferred to the "reaction" vessel where it chemically reacts in the presence of catalyst and fuel to release oxygen and heat. Both these vessels are constructed of 6-inch, schedule 80, 316 stainless steel pipe and their exterior surfaces are largely covered with band heaters. The transfer line (between vessels) and the exhaust line exiting the reaction vessel were temperature controlled with heat-tracing. In all, eight separate heating channels were used to allow good temperature control.

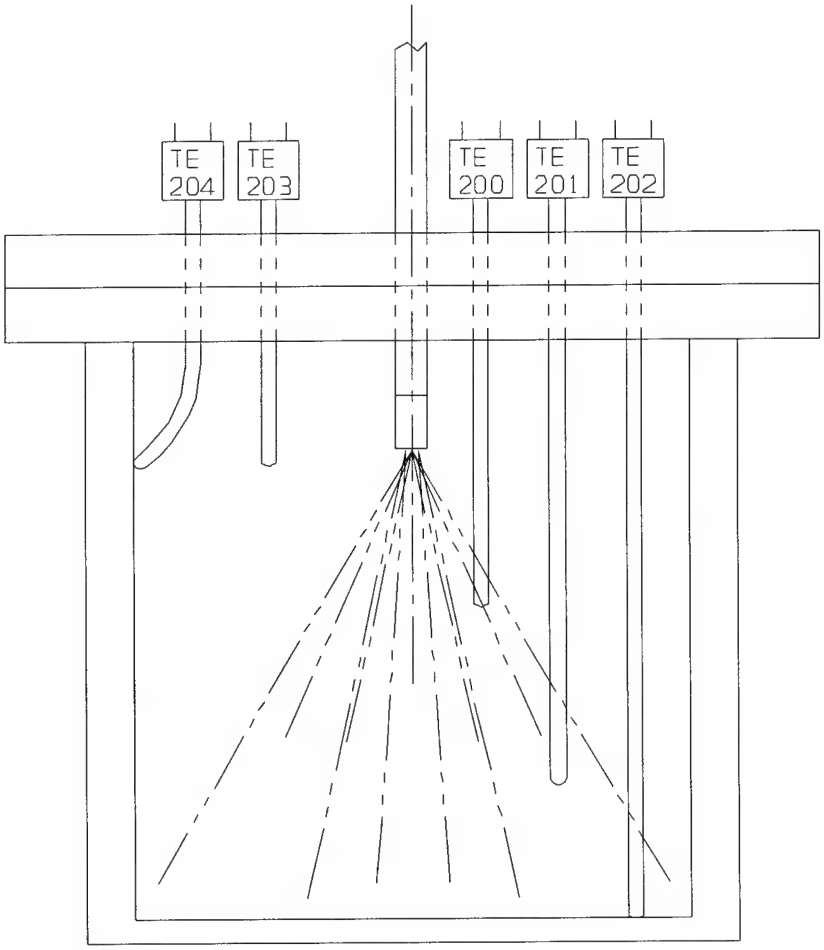


The goal is to heat the storage vessel to a temperature above the melting point of the perchlorate and heat the reaction vessel to the temperature desired for the test. Then the

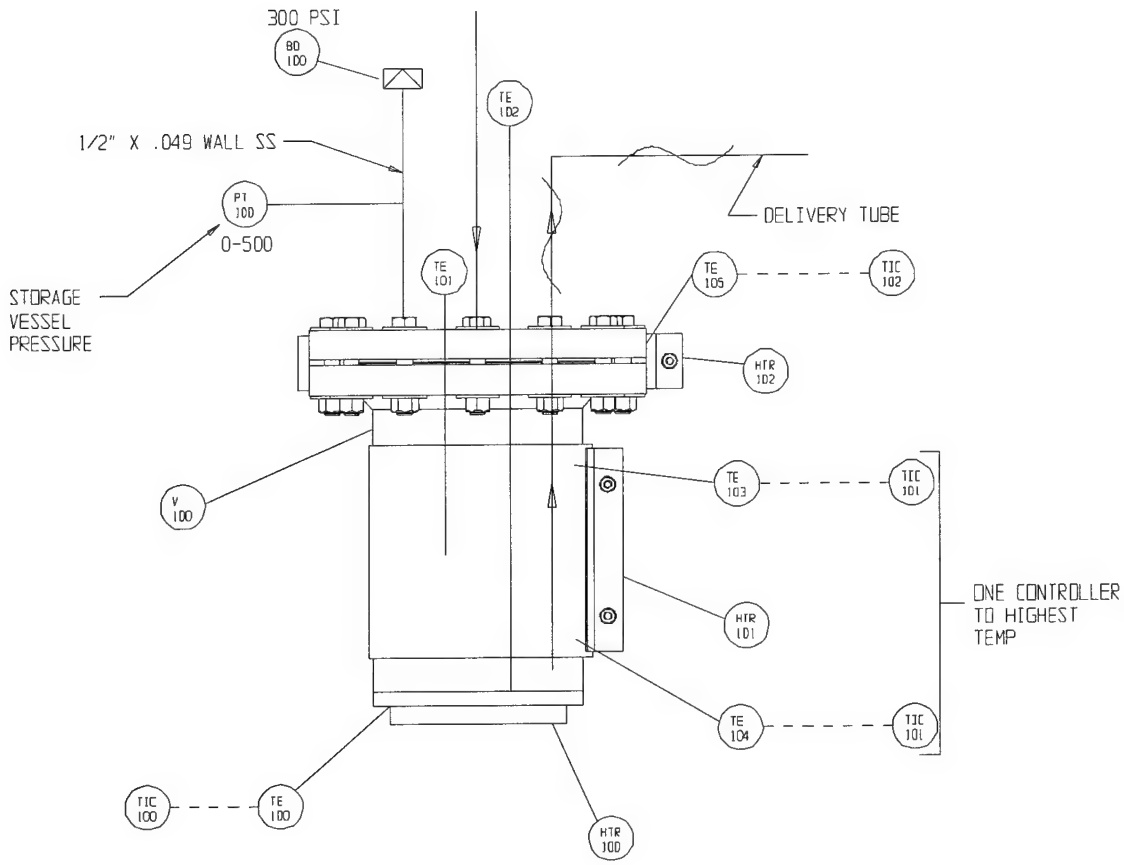
perchlorate will be pushed, using dry nitrogen gas, over to the reaction vessel where it sprays through a nozzle into the reaction vessel. The nitrogen gas pressure will be controlled to maintain the desired pressure drop (and perchlorate flow) across the injection nozzle.

The vessels are instrumented with thermocouples and pressure transducers at key locations. At the storage vessel four exterior and two interior thermocouples monitored temperature. The reaction vessel was instrumented with five exterior and five interior thermocouples. Both vessels had overpressure protection afforded through preset pressure-relief valves and burst-disks.

All temperature and pressure readings were recorded using a data-logger networked to a computer. The data-sampling rate used was 30-seconds during apparatus preheating and 2-seconds during oxygen generation.



REACTION VESSEL THERMOCOUPLES



STORAGE VESSEL

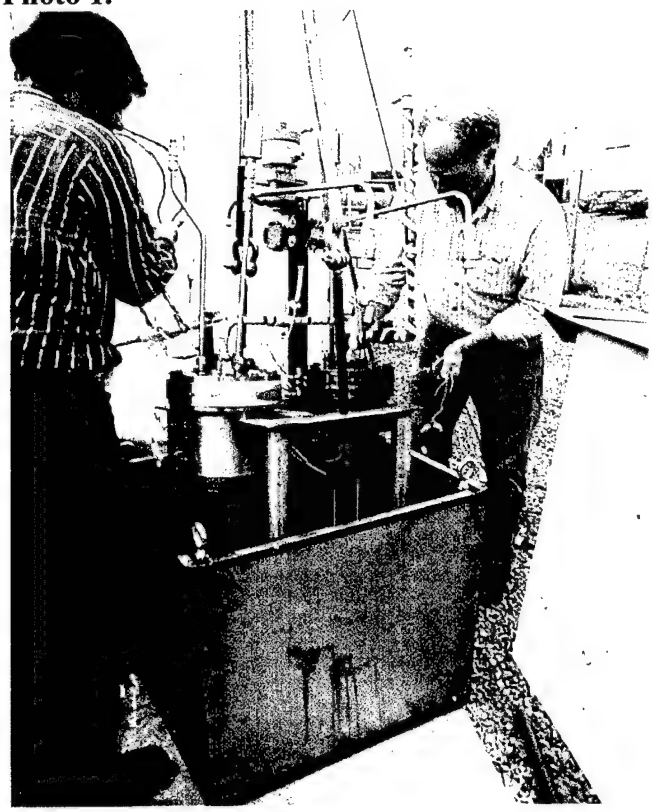
Previous testing at ARL had encountered plugging problems in the exhaust line. The current test apparatus was designed with minimal exhaust piping length along with a simplified flow-measuring section to lessen plugging problems. The goal of flow measurement was to capture gross flow behavior – high accuracy was not required. The flow metering element was a simple orifice plate welded to the end of a 1-inch tube. The flow rate was monitored through the use of a differential pressure transmitter.

The test apparatus was placed into a steel box prior to testing. This box was then filled with perlite insulation. The exposed exhaust stack was insulated with fiberglass pipe insulation. This method of insulation proved very effective and allowed rapid turnaround of the experiment.

Because of the safety concerns of the oxygen production process and some potential for a runaway reaction, the experiments were conducted outdoors. For even greater safety, the apparatus was placed in a cement lined pit during test runs.

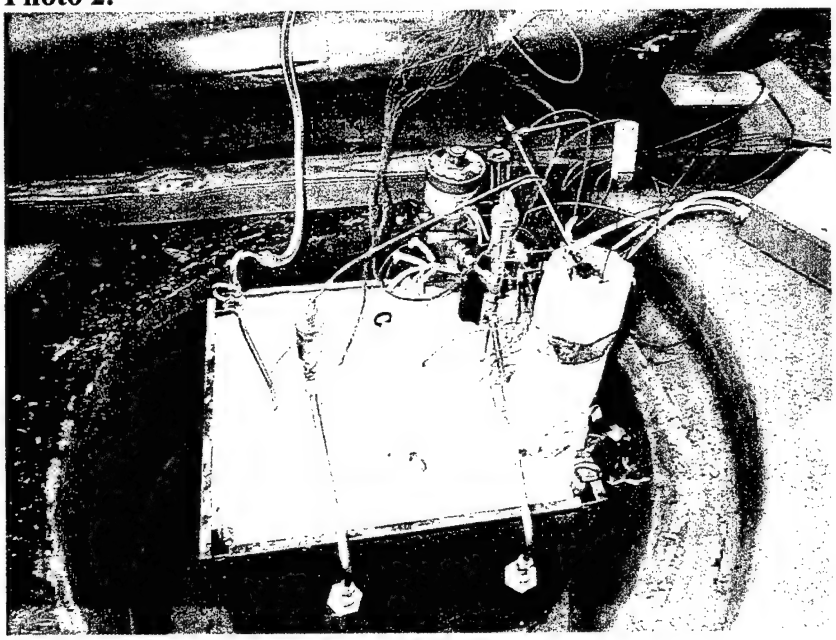
This photograph shows the apparatus being placed into the insulation containment box.

Photo 1.



This photograph is of the test apparatus, in the pit, with insulation and ready to operate. The burst-disks are in the hexagon-shaped fittings directed downward into the pit.

Photo 2.



4.2 Tests Conducted

The oxygen generator was tested five times. All but one of these tests was successful. A chronological summary of the oxygen generator tests follows. To document the results of the tests, charts of key vessel temperatures and pressures were constructed. These charts are included within the test summaries.

Test 1. (Feb. 12, 2002)
This test run was to investigate the catalytic action of lithium oxide at relatively low temperature. The reaction vessel was seeded with 25g of Li_2O (about a 2mm layer in the bottom of the reaction vessel) and the storage vessel filled with 2-kg of lithium perchlorate. The storage vessel was heated to melt the perchlorate. Heating continued until the perchlorate and storage vessel were both at a uniform 600°F. At the same time the reaction vessel was being heated to 1,000°F. After reaching the desired temperatures the test was started. The transfer of perchlorate from the storage to reaction vessel resulted in an immediate liberation of oxygen. The oxygen flow continued throughout the entire perchlorate transfer – ending when the perchlorate flow stopped due to the depletion of the perchlorate in the storage vessel. Note that some perchlorate remains in the storage vessel at the end of an experiment due to the transfer tube's position 0.5-inch above the bottom of the storage vessel.

Oxygen was produced at a rate of approximately 80g/min for about 8 minutes. Analysis of the data indicated some temperature variation within the reaction vessel at the start of the perchlorate transfer. The maximum reaction vessel thermocouple reading was 1045°F (somewhat above the desired 1000°F temperature, but still low enough that spontaneous oxygen generation should not have occurred if the lithium oxide catalyst had not been present).

At the test's conclusion, chemical deposits (lithium chloride) were found in the flow orifice. The final orifice diameter had been reduced from 0.281 to about 0.23 inches.

Chart 1. shows interior storage vessel and reaction vessel temperatures during the test. The storage vessel temperatures (100 series) remain constant near 600°F during the test, as expected. The reaction vessel temperatures (200 series) immediately jump up from the near 1,000°F starting condition when the perchlorate flow is initiated. The highest temperature recorded is the temperature (TE 202) in the bottom of the reaction vessel. This temperature would result primarily from the lithium chloride deposited in the bottom of the reaction vessel. The reason for the initial temperature rise in all thermocouples followed by a slow decrease in all but the bottom thermocouple readings is unknown at this time.

Chart 2. shows the pressure differential across the perchlorate transfer nozzle and the pressure differential across the oxygen flow orifice. The nozzle pressure drop indicates the relative rate of perchlorate transfer to the reaction vessel. The orifice

Chart 1.

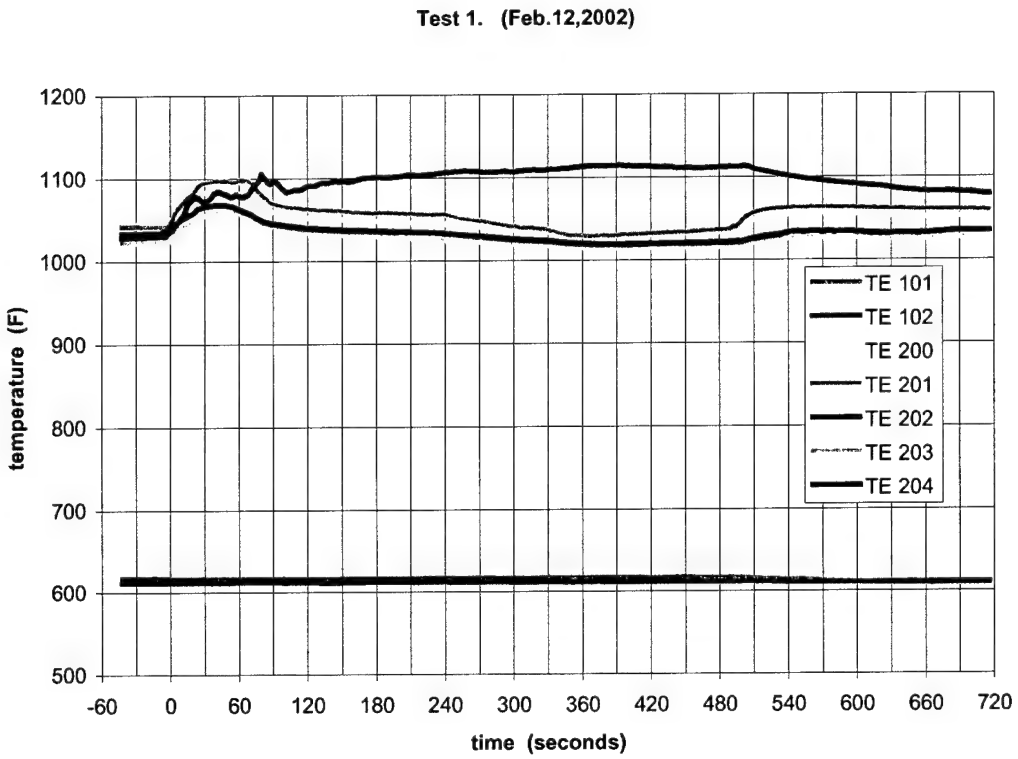
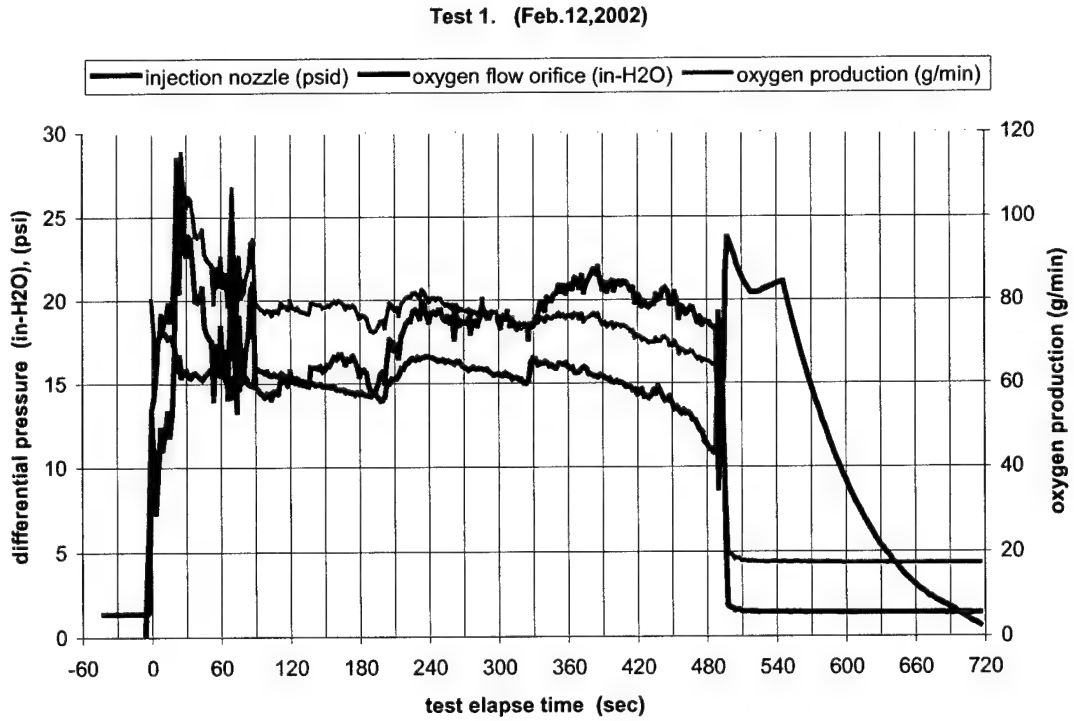


Chart 2.



pressure drop reveals relative oxygen production. Note that actual flow rate for both the nozzle and the orifice is proportional to the square root of the pressure difference. Oxygen production was computed for this run (only) and is shown on this plot. For this computation the orifice diameter was assumed to be reduced linearly with time from the initial clean nozzle to the final partially plugged nozzle. The nozzle pressure drop is manually controlled which accounts for the 'stepped' adjustments to maintain approximately 15 psid. When the perchlorate flow was complete (about 480 seconds) the pressure was first allowed to increase then was bled off manually. The oxygen flow rate was quasi constant (after the first 100 seconds or so) at about 80 grams per minute. The Charts in this same basic format (less oxygen production) are included within each test's discussion.

Test 2. (Feb. 14, 2002)

This test was to validate (with the current test apparatus) earlier testing at ARL that a reaction vessel temperature must be near 1200°F before sustained oxygen generation will occur without a catalyst when using 600°F molten lithium perchlorate as the feedstock.

This test was aborted when molten perchlorate transfer was attempted but no flow was achieved. A plugged check-valve in the transfer line was determined to be the cause. The test apparatus design was henceforth evaluated, and the check-valve was deemed unnecessary and removed. In all further testing no check-valve in the transfer line was used. The plugged check-valve may have been due to a broken heat-tape causing a localized cold spot where the perchlorate was a solid rather than liquid. This test was not repeated due to time constraints. The expected outcome was that no oxygen generation would take place.

Test 3. (Feb. 18, 2002)

This test was to investigate the use of manganese powder as a fuel along with the lithium oxide catalyst. For this test both the storage vessel and reaction vessel were heated to 600°F, the idea being that the manganese fuel would heat the vessel enough that the oxygen generation reaction could be sustained The storage vessel again contained 2-kg lithium perchlorate. The reaction vessel held 25g of lithium oxide and 134g of manganese powder. The reaction vessel had been loaded through a small ½-inch diameter port; consequently, the manganese powder probably formed a mound fully covering the lithium oxide added first. An attempt was made to spread the fuel and catalyst by stirring with a rod through the fill port.

When perchlorate was transferred to the reaction vessel, an immediate reaction with the manganese powder occurred – rapidly increasing the interior temperate. The peak reaction vessel interior temperature recorded was 1360°F at 15 seconds

after perchlorate flow began. This was the thermocouple located in the bottom of the vessel. All the thermocouples showed some response to the reaction. The rapid increase in temperature initiated oxygen flow out of the system in addition to the oxygen used to burn the manganese. Oxygen flow continued for approximately 2-minutes before plugging at the injection nozzle prevented further perchlorate transfer (reference Chart 3. and Chart 4. for specific temperature and pressure data). The reason for the nozzle plugging was not immediately apparent but later it was surmised that the high temperature had begun some decomposition of the perchlorate before the injection nozzle which would produce lithium chloride, a solid at that temperature. Upon disassembly, a blackish, hard metallic-like layer was found in the reaction vessel beneath a softer tan layer. Photo 3. shows the reaction vessel (post test) before cleaning, with the tan layer visible.

Photo 3.

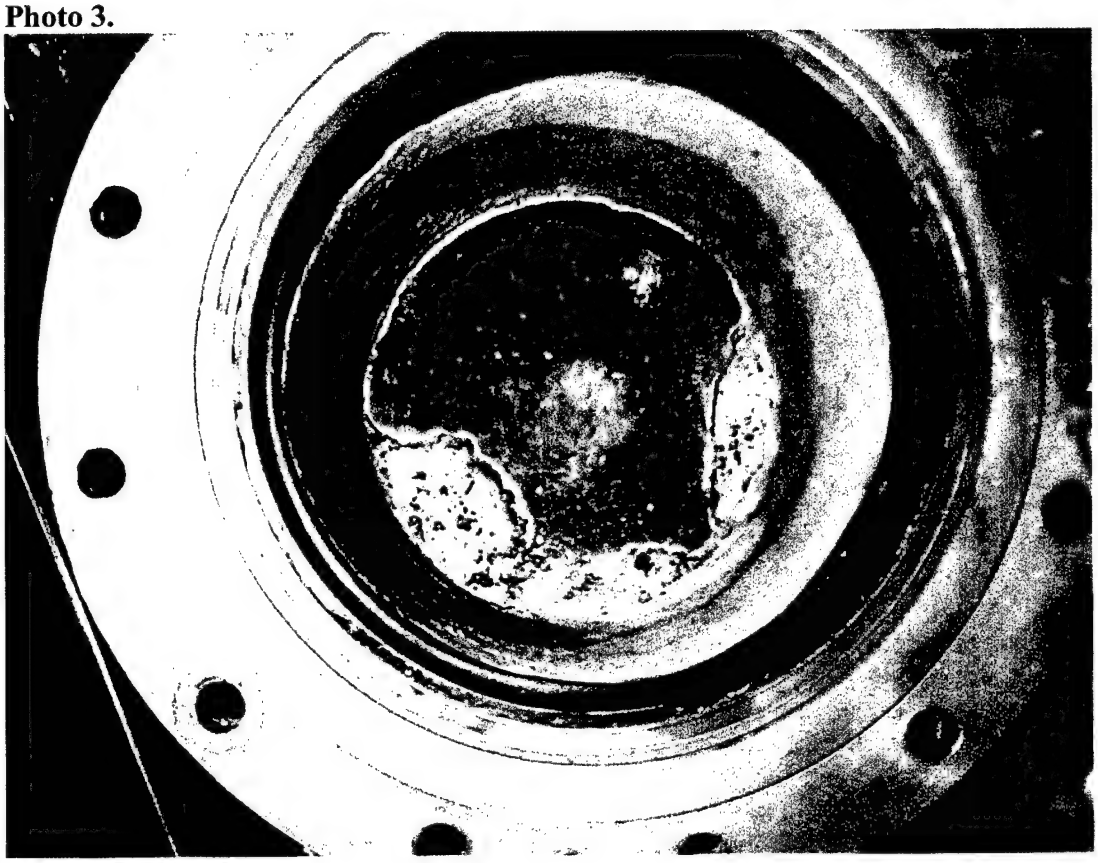


Chart 3.

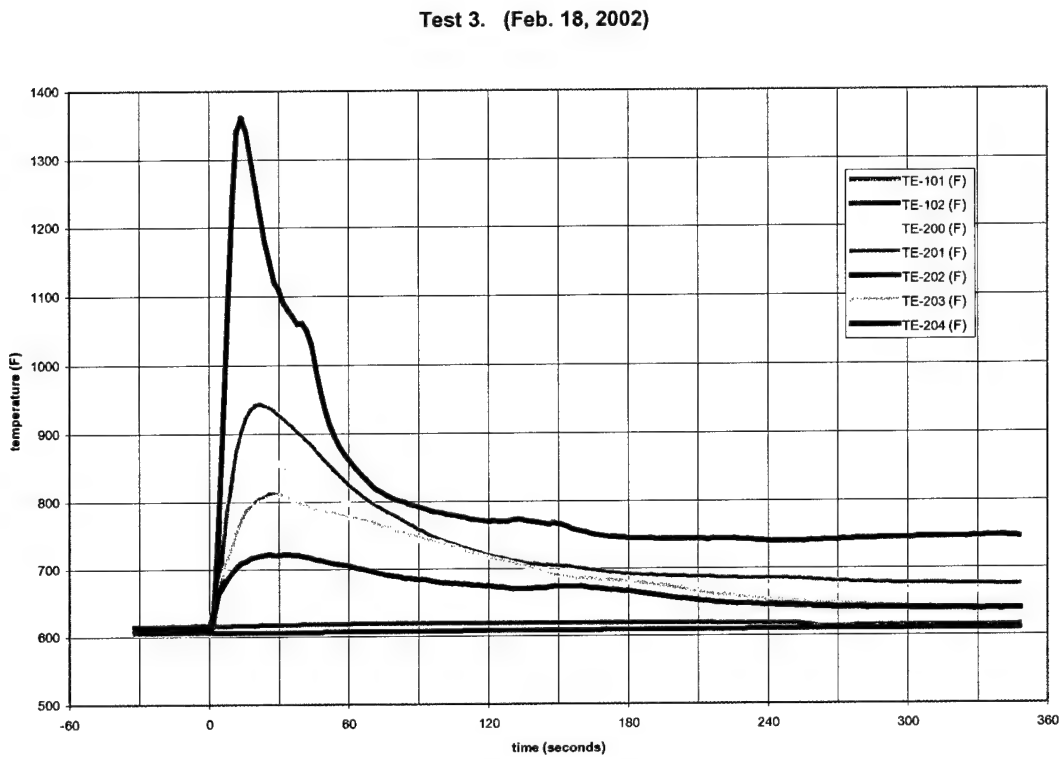
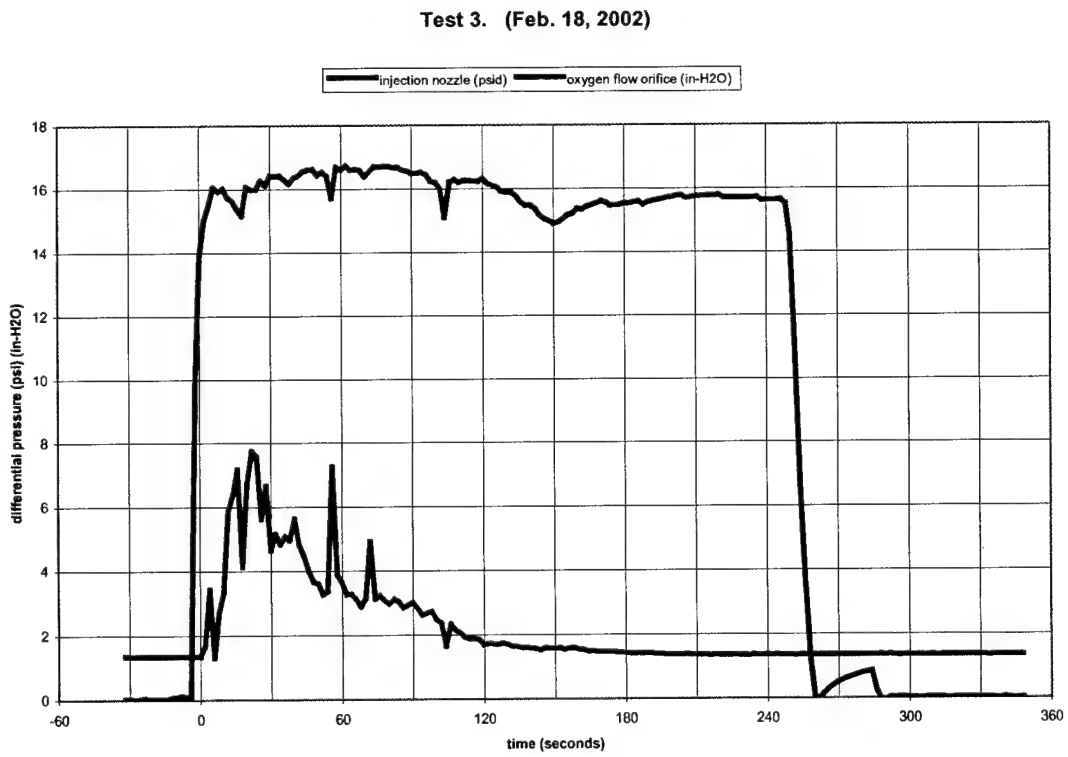


Chart 4.



Test 4. (Feb. 19, 2002)

This test was a repeat of test 3 – 25g lithium oxide and 130g manganese powder. The loading of the reaction vessel was done with the lid off and the lithium oxide and manganese powder were mixed and uniformly spread over the bottom of the vessel. The quantity of manganese used was sufficient to completely cover over the lithium oxide. Hence the initial perchlorate transferred likely encountered manganese before lithium oxide granuals were exposed as the test progressed. A new injection nozzle in the reaction vessel was used to lessen the likelihood of unintended plugging.

Upon perchlorate transfer, reaction vessel interior temperature quickly spiked to over 2100°F. More vigorous oxygen flow was measured (than witnessed in test 3.), but again after about 2-minutes, the injection nozzle plugged. Photo 4. shows the reaction vessel lid with plugged nozzle at post run disassembly. The reaction vessel contain a roughly 2-inch deep layer of porous and somewhat spongy material shown in Photo 5. The hard metallic-like layer bonded to the bottom of the reaction vessel in test 3 was not evident in this test run – suggesting that all of the manganese had reacted before nozzle plugging occurred. The higher temperature reached within the reaction vessel during test 4 (+700°F over test 3 reaction vessel temperature) further supports this conclusion. The temperature and pressure data gathered during this test run are shown in Chart 5. and Chart 6., respectively.

Photo 4.

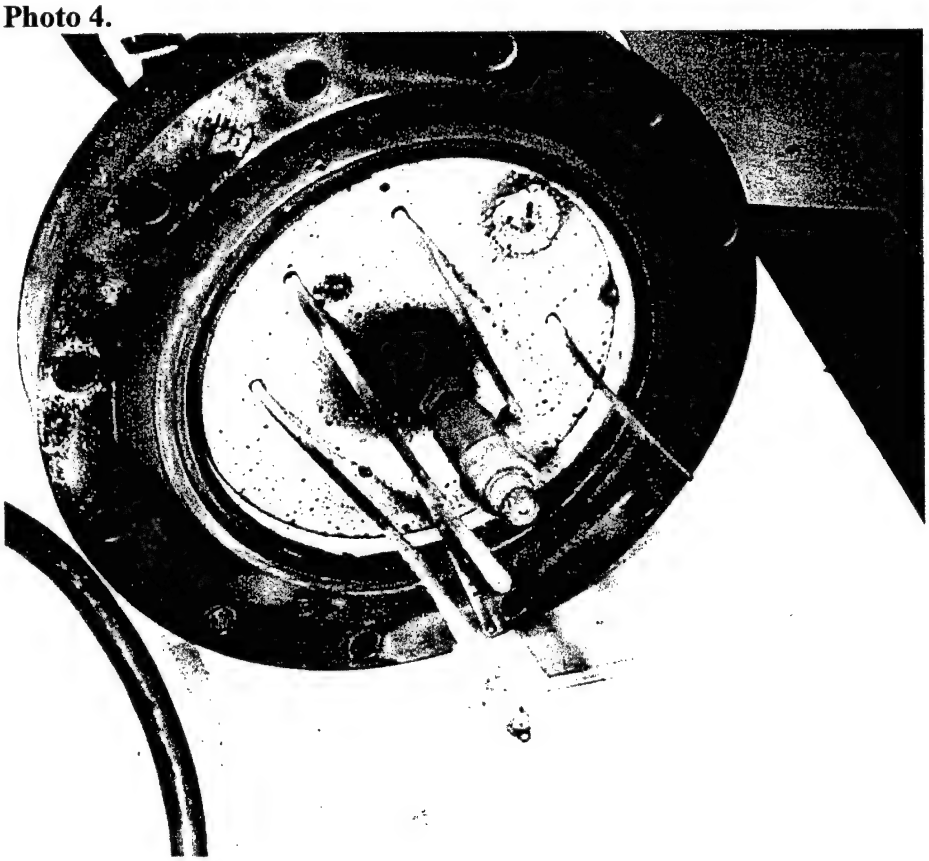


Photo 5.

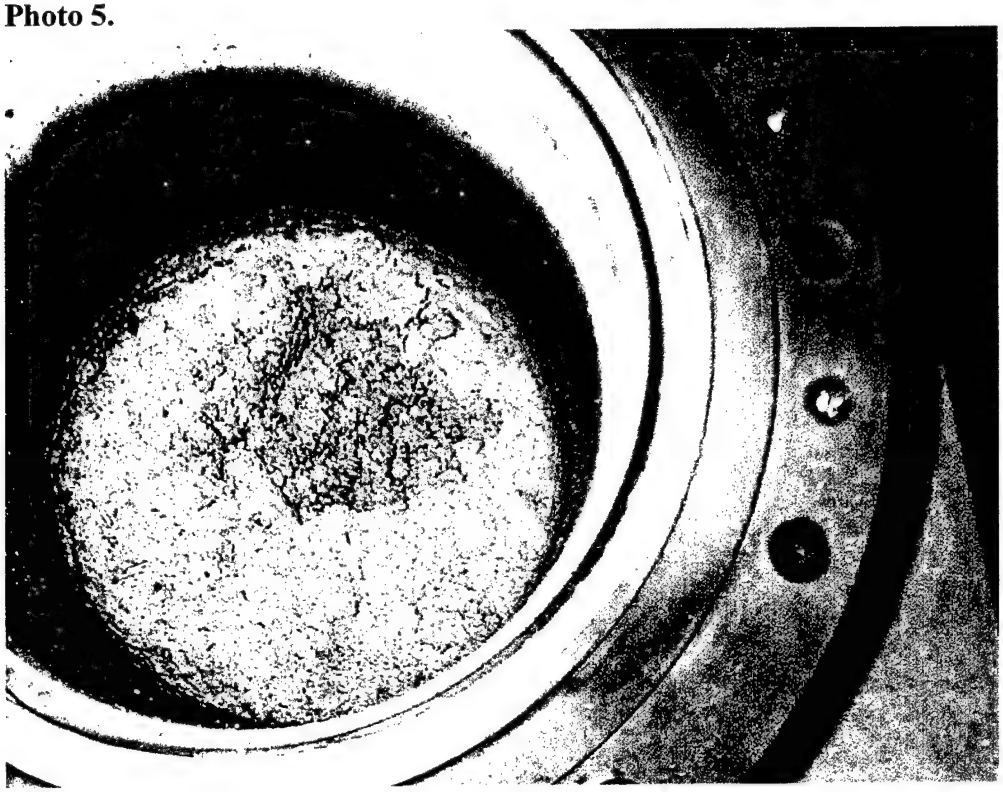


Chart 5.

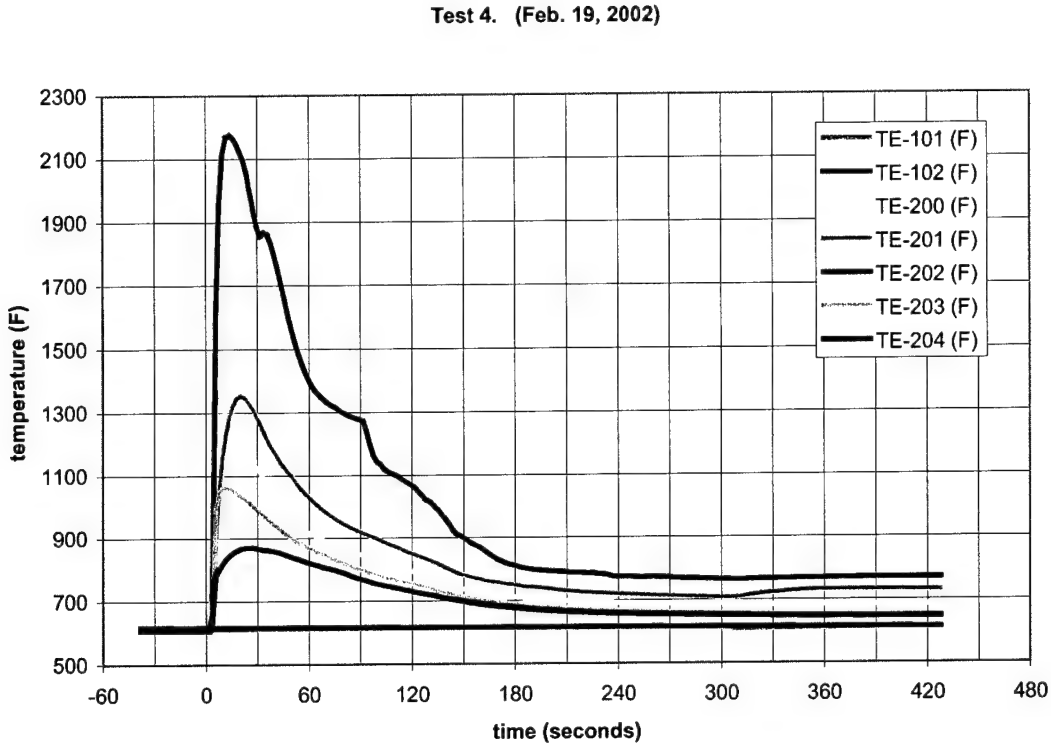
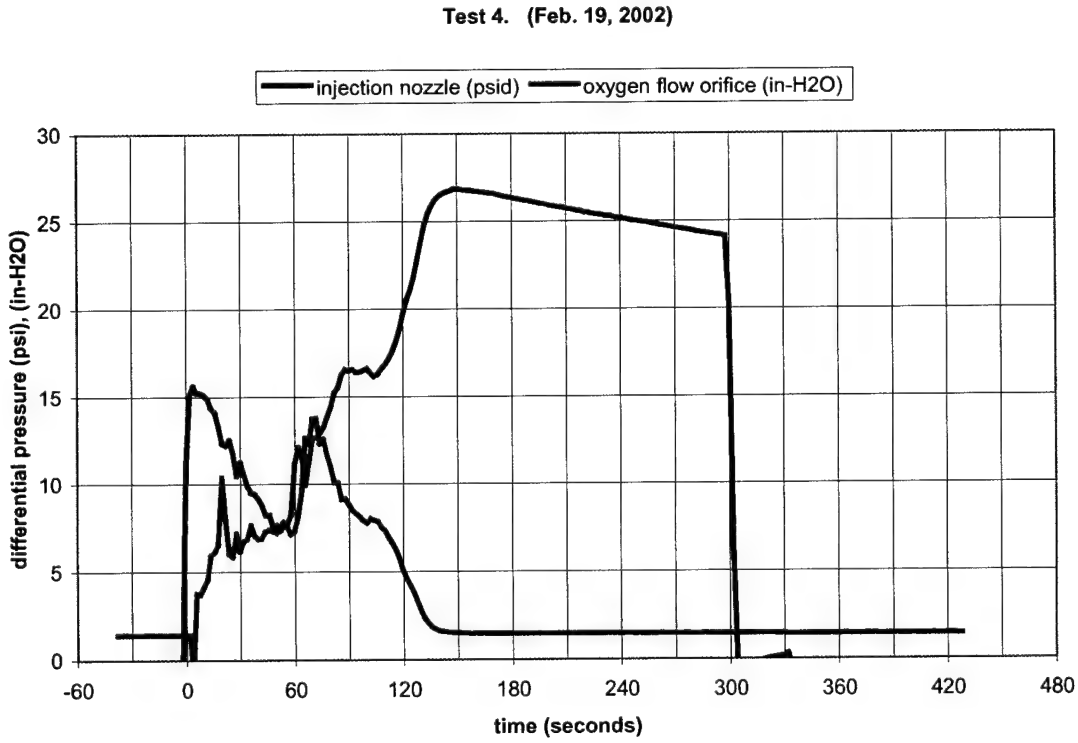


Chart 6.



Test 5. (Feb. 21, 2002)

This test was essentially a repeat of test 1 (25g of lithium oxide in reaction vessel). The key difference was to more closely match the desired 1000°F reaction vessel starting temperature. The maximum reaction vessel thermocouple reading was still slightly high but now just 1018°F at the start of the experiment. This test began with a larger perchlorate load in the storage vessel (3-kg)

When the 600°F molten perchlorate was sprayed into the reaction vessel, oxygen generation began immediately. The rate of oxygen generation grew slowly during the first 90-seconds to a maximum rate of 110g/min. Increasing the injection nozzle differential pressure from 15psid to 20psid at about 180 seconds resulted in a peak oxygen production rate of 120g/min. The flow rate then decreased when the injection nozzle pressure differential was reduced back to 15psid at 300 seconds. Significant buildup of deposits in the flow orifice was observed at the conclusion of the run. Final orifice diameter had been effectively reduced from its initial 0.281-inch diameter to approximately 0.15-inch diameter. That probably accounts for the increasing differential pressure across the flow orifice, particularly after 570 seconds. The disassembled reaction vessel contained a dense layer of lithium chloride shown in Photo 6. The temperature and pressure data gathered during this test run are shown in Chart 7. and Chart 8.

Note that in this test two thermocouples failed. This is probably due to the high temperatures encountered in the previous test (test 4). One failed thermocouple was in the storage vessel (TE 102) and therefore TE 104, which is on the outside of the storage vessel was substituted on the temperature plot. The other failed thermocouple was TE-204. This reading was eliminated from the plot.

Photo 6.

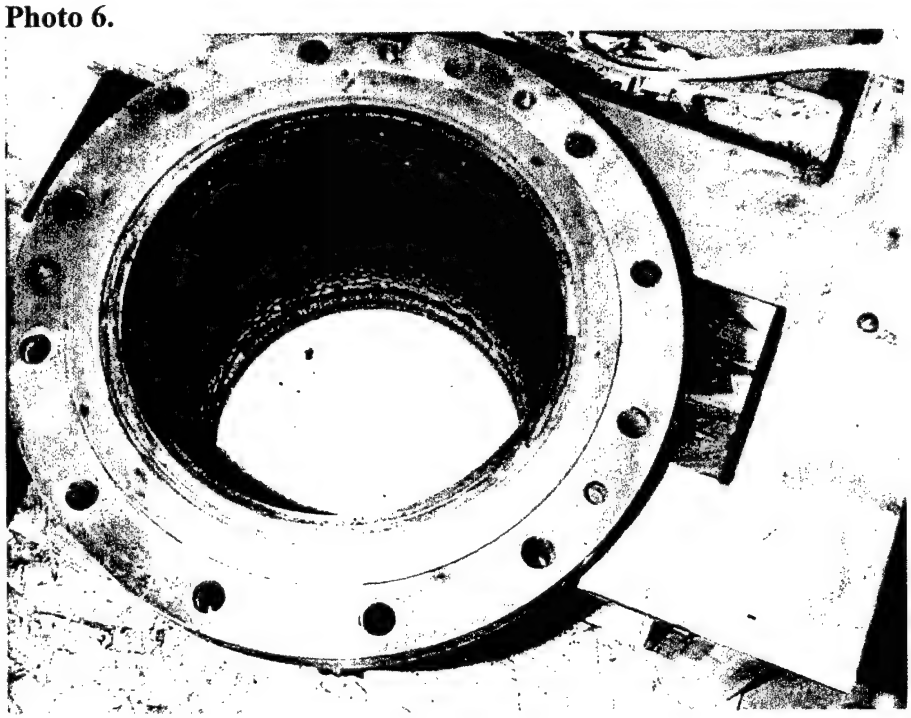


Chart 7.

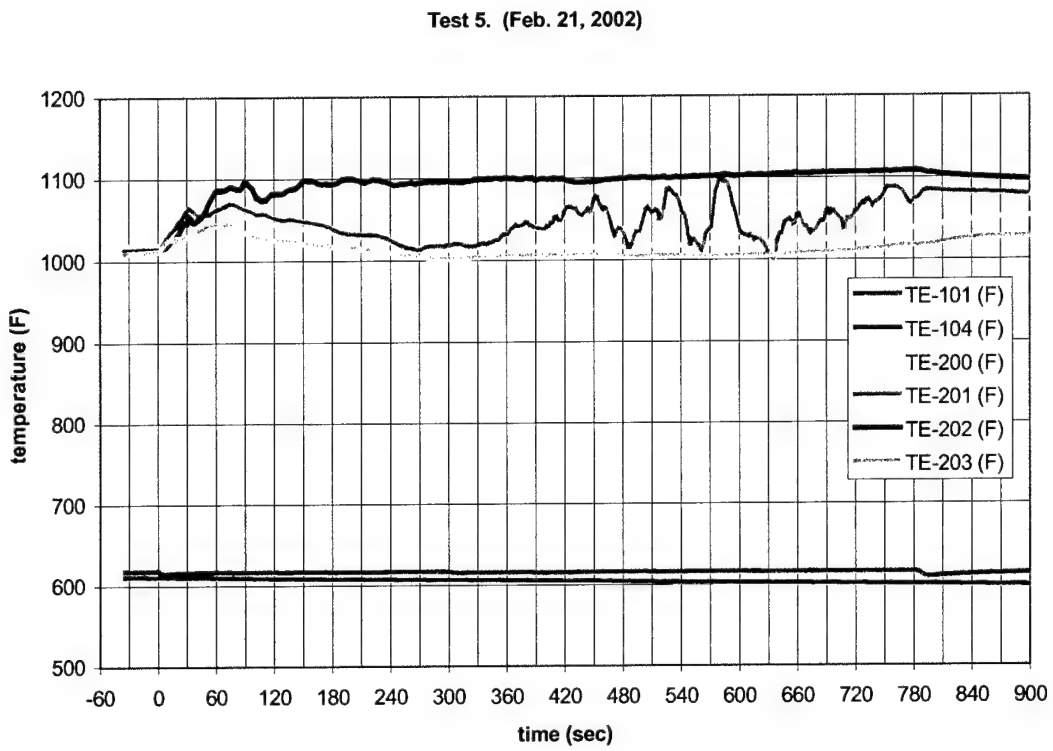
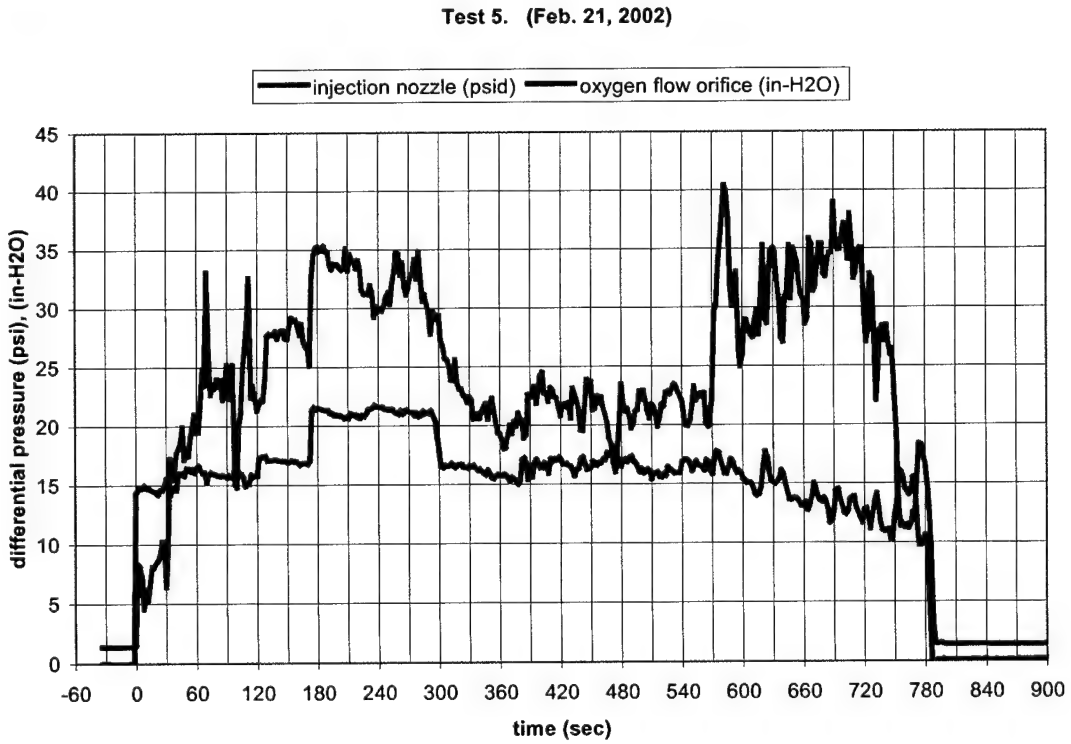


Chart 8.



4.3 Comments

At the end of all oxygen generator test runs, significant chemical deposits remained in the reaction vessel. These deposits would ultimately limit the duration of the test that could be run. The exhaust / flow orifice section also accumulated deposits during oxygen generation – partially closing off the flow orifice. The gradual plugging of the flow orifice (during oxygen generation) results in the flow measurement containing considerable uncertainty. Oxygen flow estimates for the initial moments of the test would be the most accurate with estimate accuracies degrading as the test progressed.

For the tests using manganese (which resulted in injection nozzle plugging), calculations made using nozzle pressure-drop data early in the test would yield the most accurate perchlorate flow estimates.

In all tests, the thermocouple data should be accurate with possibly one exception. The lowermost thermocouple at the end of the highest temperature tests (with manganese) had the stainless steel sheath melted away – exposing the thermocouple's tip. Even so, the temperature data from this thermocouple seems reasonable.

The current test-apparatus is not of an appropriate design for long-duration steady-state oxygen production. The test-apparatus used was adequate and useful in assessing the value of lithium oxide catalyst and manganese as a chemical heat source.

5. DISCUSSION OF EXPERIMENTAL RESULTS

The experimental program described above successfully demonstrated the effects of two reaction vessel additives; lithium oxide catalyst and manganese fuel. The results of these experiments can be summarized as follows.

1. The decomposition of lithium perchlorate appears to be catalyzed by the presence of lithium oxide.

2. The reaction of molten lithium perchlorate and powdered manganese fuel appears to be a viable means of generating thermal energy to pre-heat the reaction vessel.

Each of these effects is discussed in more detail, below.

5.1 Lithium Oxide Catalysis

Tests 1 and 5 investigated the effects of lithium oxide alone. The results of these experiments (shown in Charts 1, 2, 7 and 8) are consistent and show that oxygen production began immediately upon initiation of perchlorate flow and proceeded until the $LiClO_4$ became exhausted. In addition, changes in the delivery pressure (the differential

pressure between the storage and reaction vessels) were reflected in the rate of oxygen production.

These results are entirely consistent with those of earlier oxygen generator tests conducted at ARL / Penn State except that the reaction vessel temperatures prior to and during these runs were considerably lower than in previous experiments. As discussed above, the reaction vessel temperatures were between 1000 and 1050 °F prior to the current test series. ARL experience has shown that these temperatures are not sufficient to sustain a steady oxygen flow without the presence of the Li_2O catalyst. All successful oxygen generator operations prior to this test series required the reaction vessel temperatures to be greater than the melting point of the lithium chloride (LiCl) product, i.e. 1130 °F. Standard ARL operating procedure requires that all reaction vessel temperatures measured 1150 °F or higher prior to initiation of perchlorate flow.

Because the lithium perchlorate spray is at a relatively cool (600 °F) temperature, it has a tendency to cool the inner walls of the reaction vessel. This effect is counterbalanced by the exothermic nature of the decomposition process (Reaction [3]). If the rate of the decomposition reaction is too low, the cooling effect will dominate and the spray will "quench" the inner surfaces of the reaction vessel, shutting down oxygen production and allowing perchlorate to build up in the reaction vessel. In earlier ARL testing, reaction vessel temperatures below 1130 °F were not sufficient to sustain a high rate of decomposition, resulting in quenched conditions.

The results of the present test series indicate that lithium oxide acts as a catalyst, increasing the rate of perchlorate decomposition. This ultimately allows oxygen generation to proceed at lower temperatures. As discussed in an earlier section, a lower reaction vessel temperature has a number of practical advantages including reduced parasitic heat losses and simplified handling of the lithium chloride product.

5.2 Manganese fuel

Tests 3 and 4 investigated the effects of manganese fuel. The results of these experiments (shown in Charts 3, 4, 5 and 6) show a large temperature spike at the inception of perchlorate flow, indicating a reaction between the molten $LiClO_4$ and powdered Mn.

Previous experiments at ARL / Penn State investigated the reaction between molten perchlorate and aluminum powder. Those experiments showed that the $Al/LiClO_4$ reaction proceeds very slowly until the perchlorate begins to decompose rapidly (i.e. 1000 – 1200 °F). The results of the current program indicate that Mn is a more suitable fuel in that it reacts at relatively low (600 °F) temperatures.

The significance of this result is that manganese fuel can be used to "boost" reaction vessel temperatures from 600 °F to 1000 °F at the start of oxygen production. This

would simplify the startup process in a practical system, since the reaction and storage vessels could be pre-heated to the same 600 °F temperature.

Note that tests 2 and 3 ended when the delivery system became plugged. It appears that the high temperatures in the reaction vessel resulted in overheating of the injection nozzle, causing perchlorate to decompose and plug the small nozzle flow passages with LiCl. This conclusion is tentative, pending chemical analysis of material taken from the interior of the delivery tube and nozzle.

5.3 Suggestions for Future Experimental Work

The results of this program must be quantified in more detail before the Li_2O and Mn additives can be used in a practical oxygen generator. A future experimental program should address the following issues.

1. Lithium oxide appears to catalyze the decomposition of lithium perchlorate, but the effects of temperature need to be investigated in more detail. A series of experiments should be carried out to determine the lowest possible operating temperature for a practical Li_2O-catalyzed reaction vessel.

2. In the present series of tests, lithium oxide powder was scattered loosely on the bottom of the reaction vessel. Alternate means of utilizing this material should be investigated to realize the greatest benefit from its catalytic effect. Options include extended surfaces or packing materials coated with lithia ceramic.

3. Manganese powder placed in the reaction vessel prior to the experiment reacts with lithium perchlorate at 600 °F. In order to develop a practical system, it will be necessary to develop ways to position the Mn fuel so that the heat from this reaction will be distributed over the entire interior surface of the reaction vessel. A sintered Mn liner might be possible.

4. The very high peak temperatures of the Mn / $LiClO_4$ reaction apparently overheated the spray nozzle in tests 2 and 3. Methods to prevent this effect must be investigated. Options include active cooling and/or radiation shielding of the nozzle, or distribution of the Mn fuel to reduce peak temperatures.

6. PROPOSED OXYGEN GENERATOR FOR UUV

Figure 5 is a schematic diagram showing a system sized to address requirements N001-T005 "Oxygen Source for Underwater Fuel Cells." While this notional design accounts for the weights and volumes of all of the major oxygen generator components, a more detailed design process is required before this system could be produced in practice. Components are drawn approximately to scale. A 21-inch long section of a heavyweight torpedo-sized shell is required for this device.

The major oxygen generator components and subsystems shown in Figure 5 are discussed briefly below. Table 1 summarizes the results of the sizing study used to generate the sketch.

The largest component is the **Storage Vessel**, which is designed to hold 183 pounds of lithium perchlorate, enough to generate 110 pounds (50kg) of oxygen gas. Thin copper fins are used to transfer heat from a lithium-fueled energy source (discussed below) to the $LiClO_4$.

As shown, the cylindrical Storage Vessel has an 18-inch OD and 0.25-inch wall thickness. Since fuel cells require a low-pressure source of oxygen, this construction should be very conservative. Although the lithium-fueled energy source acts to carry part of the axial pressure load, it is likely that additional tie rods will be needed in order to use flat end plates as shown. A more detailed structural analysis is required.

The **Lithium Fueled Energy Source** (LFES) is a small (6.75-inch ID) cylindrical reactor mounted to the side, but concentric with the Storage Vessel. Within the LFES the lithium / sulfur hexafluoride (Li / SF_6) reaction generates heat to melt the $LiClO_4$ and bring it to its initial temperature of 600 °F. Approximately 8.4 pounds of lithium are required to provide the initial heating and to make up for heat lost to the environment over the course of system operation. As discussed above, fins are used to transfer heat from this reactor to the bulk of the perchlorate. In practice, these fins are made of thin copper sheet metal, plated with nickel for corrosion resistance, and shrink-fitted to the outside of the reactor. This approach has been used in several oxygen generator designs at ARL / Penn State. To date, embedded lithium-fueled reactors have been used to controllably melt up to 100 pounds of lithium perchlorate.

The **Delivery Tube** is used to transfer molten $LiClO_4$ from the bottom of the Storage Vessel to the Reaction Vessel. A spray nozzle in the top of the reactor distributes the perchlorate over the active surface of the reactor. Note that the Storage Vessel is pressurized with a small quantity of oxygen gas to force the molten perchlorate through the Delivery Tube and spray nozzle.

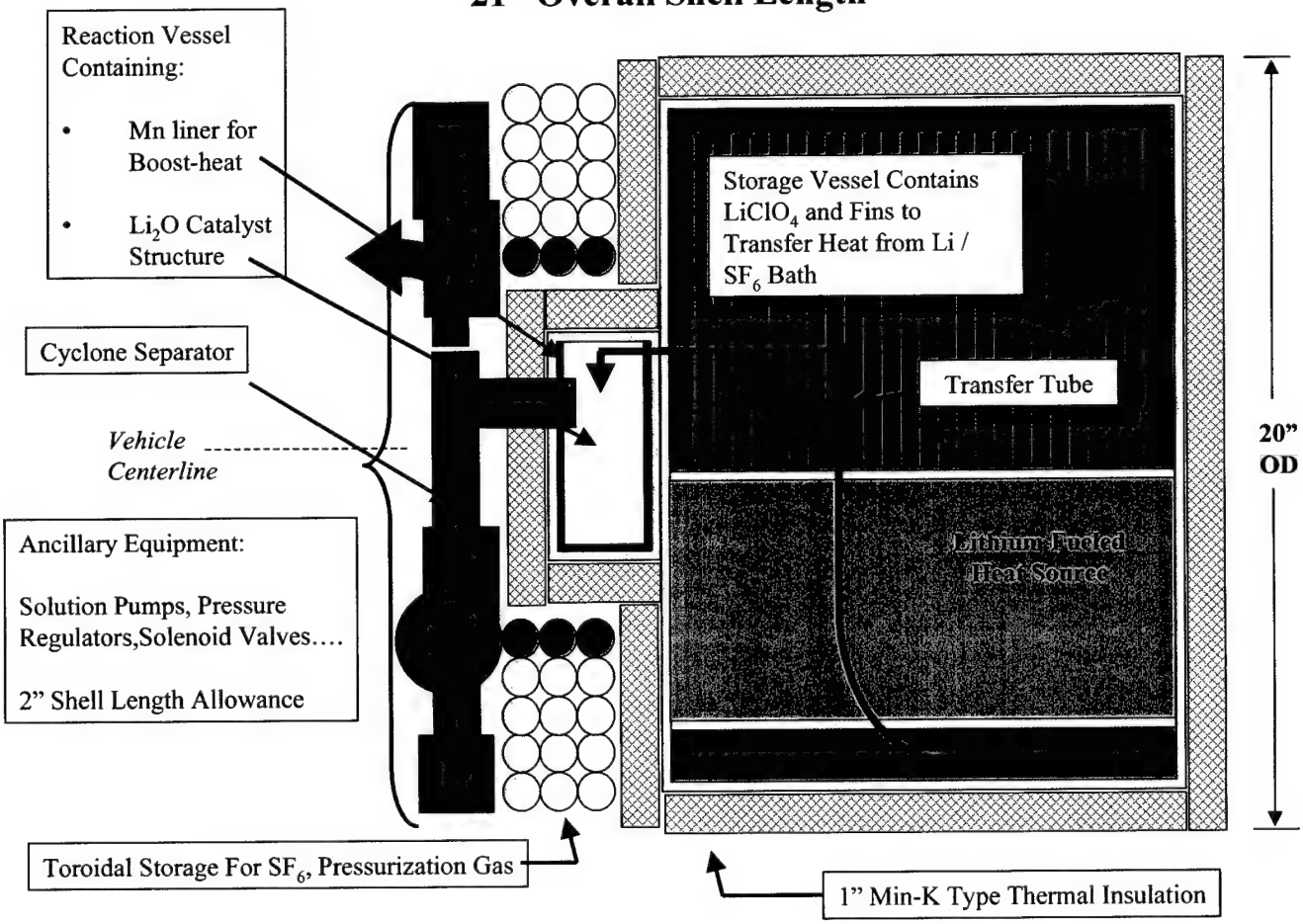
Oxygen production takes place when the molten lithium perchlorate decomposes in the **Reaction Vessel** (see Reaction [3]). The Reaction Vessel contains a small quantity of **Manganese Fuel**, which pre-heats the reactor surfaces from 600 °F to its operating temperature. This chamber also contains **Lithium Oxide**, which catalyzes the

decomposition of the perchlorate, allowing the reaction to take place at a temperature below the melting point of the LiCl product. As discussed in a previous section of this report, further experimental work is needed to determine the optimum Reaction Vessel temperature, but at this time it appears that the oxygen can be produced at 1000 °F.

In practice, the manganese fuel may be in the form of a sintered liner that distributes the heat from the Mn/ $LiClO_4$ reaction evenly across the Reaction Vessel surface. The lithium oxide catalyst may be in the form of fins, packing or other extended surfaces coated with lithia ceramic.

Two gases are required, sulfur hexafluoride (to react with the lithium fuel) and a pressurization gas (to force the $LiClO_4$ through the delivery tube and spray nozzle). **Toroidal Storage** coils made from 1" tubing provide efficient storage for these gases.

Figure 5: Notional UUV O_2 Generator Design Cross Section: 21" Overall Shell Length



As shown in Figure 5, a small **Cyclone Separator** is used to effect separation of the solid particles of lithium chloride from the oxygen stream. This device is based on a design developed and demonstrated at ARL for removal of aluminum oxide from high temperature mixtures of steam and hydrogen (Miller, 2001). The chloride is dissolved in water and pumped overboard by a small positive displacement pump.

A small amount of energy is required to drive the pump. At a depth of 1500 feet, approximately 50 W (.07 Hp) of electricity would be consumed. It is likely that other UUV subsystems will incorporate pump(s). For example, it may be necessary to circulate seawater for cooling the PEM fuel cell stack and/or electronic components. It should be possible to combine these functions with product removal, thereby reducing the overall complexity of the system.

In addition to removing the entrained lithium chloride product, the cyclone separator cools the hot oxygen gas stream. The separator acts as a direct contact heat exchanger, transferring thermal energy from the gas stream to the scrubbing water.

Note that the products discharged overboard are liquid. There is no gaseous wake, which reduces the noise signature of the system. Although a chemical wake is produced, high ambient background levels of the constituent ions (Li^+ and Cl^-) would make detection of this chemical wake very difficult.

The entire apparatus is covered with **Insulation** to reduce heat loss. A convective heat transfer model suggests that the apparatus will continuously lose approximately 600 W of energy during operation. This heat loss is made up as necessary by the lithium fueled heat source reaction. The system shown in Figure 5 incorporates additional Li fuel and SF_6 oxidizer for this purpose.

A number of minor components, including two pressure regulators, two solenoid valves, several explosive valves, an oxygen metering valve, etc. are required. In Figure 5, an allowance of 2" of shell space (a volume of approximately 630 cubic inches) is provided. In practice, the packaging of these components would be optimized along with the remainder of the UUV powerplant.

Table 1, below, presents estimates of the weights of individual system components. The total estimated weight is approximately 470 lb (213 kg) for a system sized to deliver 50 kg of oxygen. Thus, the oxygen storage efficiency on a mass basis is 0.23 pounds oxygen per pound of system.

As discussed above, the oxygen generator occupies a 21inch length of shell, assumed to have an effective internal diameter of 20 inches, for a total volume of 6600 cubic inches. The effective oxygen storage density of this system is therefore .017 pounds oxygen per cubic inch. As shown in Figure 1, this exceeds the density of 5000 psi oxygen gas, even if the weight and volume of the high pressure gas cylinder is neglected. It approaches the storage density of 90% H_2O_2, again neglecting the tankage, storage losses, insulation, etc. required for a practical peroxide-based system.

Table 1: Weights of System Components

Component	Approximate Weight (lb)	Notes
Expendables:		
Lithium Perchlorate	183	Delivers 50 Kg of oxygen gas
Lithium Fuel	9	Sized to deliver pre-heat energy and make up for 600 W constant heat loss, + 25% additional lithium.
SF_6 Oxidant	18	
Pressurization Gas	1	Pressurize entire Storage Vessel to 20 psi with oxygen gas.
Pressure Vessels, Etc.		
Storage Vessel	91	18" OD x 14" LOA x 0.25" walls. Stainless steel.
Lithium Fueled Reactor	22	7.25" OD x 13.5" LOA x 0.25" walls. Stainless steel.
Fins	57	14, 16" OD, 1/16" sheet copper.
Reaction Vessel	7	6" OD x 3" LOA x 0.25" walls. Stainless steel.
Toroidal Storage Coils	28	55' of 1" OD x .049"wall stainless tubing.
Minor Components:		
Cyclone separator	2	Based on T. F. Miller design.
Solenoid valves	3	2 Al body Circle Seal valves @ 1.25 lb.
Pressure regulators	4	2 Al body Grove backpressure regulators @ 1.6 lb.
Chloride separator pump, motor	2	Based on existing micro-pump coolant pumps.
Oxygen control valve, motor	3	Based on existing ARL control valve design
Explosive valve	1	Typical Conax valve
Insulation	10	
Misc. fittings, etc.	25	Fittings, check valves, minor plumbing, etc.
Total	466	

6.1 Recharging of Oxygen Generator

As discussed above, the oxygen generator is initially filled with solid lithium perchlorate, as well as Mn fuel and lithium oxide catalyst.

If this type of device is incorporated in a UUV, it will be necessary to remove and replace the entire cylindrical assembly containing the Storage Vessel and Reaction Vessel between missions. The remainder of the plant (separator, pumps, SF_6 and O_2 storage components) can remain in place, although sulfur hexafluoride and oxygen gas must be added.

It will be necessary to open a UUV shell in order to recharge the oxygen generator. This probably requires that refueling operations take place at a shore-based maintenance activity.

Once removed from the system, the Storage Vessel/Reaction Vessel assembly can either be disposed of or recycled; ARL currently finds it economically advantageous to clean and refill similar components between experiments. Remanufacture and refill of this assembly will probably require some specialized equipment and would take place at a "D" level maintenance activity.

The reactants ($LiClO_4$, Mn and Li_2O) are solids and very stable unless exposed to high (> 500 °F) temperatures for long periods of time. The products (LiCl, MnO_2 and Li_2O) are inert and stable under all temperature conditions. None of these chemical constituents is particularly toxic in an acute sense, and none have any chronic health effects.

Safety concerns and specialized equipment requirements are likely to be lower for this proposed perchlorate-based oxygen generator than for systems that incorporate very high pressure oxygen gas, liquid oxygen, or hydrogen peroxide. Since $LiClO_4$ is stable in long-term storage, the system described above should present logistic advantages relative to options that rely on LOX or H_2O_2.

6.2 Capital and Turn-Around Costs

At this time, it is difficult to estimate the capital costs for this proposed system, as it depends strongly on the number of units produced. It should be noted that the device is fabricated from standard materials such as stainless steel, using conventional construction technologies such as TIG welding.

Turn-around costs for this unit can be estimated based on ARL / Penn State experience with similar oxygen generators. The major expendable is lithium perchlorate, which was recently quoted at $41 per kg (in 100 kg lots). This translates into a refill cost of $3,400 per 183-pound charge. It should require approximately two-man weeks of effort in order to clean out, refill and reassemble an oxygen generator unit. A rough estimate of total turn-around costs is approximately $10,000 per exercise vehicle.

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